

The Jahn-Teller theorem for 3d ions and their compounds

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In contrary to customarily consideration of the Jahn-Teller theorem for 3d-ion compounds in the orbital space only we point out that it has to be considered in the spin-orbital space. It is despite the weakness of the intraatomic spin-orbit coupling. A direct motivation for this paper is an erroneous claim of a recent Phys. Rev. Lett. **96** (2006) 027201 paper that the high-spin $t_{2g}^4 e_g^2$ state of the $3d^6$ configuration is not Jahn-Teller active.

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There is ongoing long-lasting discussion in the magnetic community about a relationship between the electronic structure, magnetism, the local 3d-ion surrounding and a (off-cubic) lattice distortion in 3d ionic compounds like LaMnO_3 , LaCoO_3 or YTiO_3 . In this discussion terms like the Jahn-Teller (J-T) effect and the J-T distortions unavoidably appear which obviously are related to the J-T theorem. This long-lasting theoretical discussion reveals that the physical picture for 3d-ion compounds is far from being established. On other side, experiments, e.g. X-ray-absorption fine structure (XAFS) experiments provide more and more accurate data on the local surrounding at the atomic scale which are generally discussed in connection to the J-T effect. The aim of this short Letter is to put an attention that the physically adequate degeneracy space for the consideration of the J-T theorem for the 3d ions is the spin-orbital space. It is in contrast to the current literature that considers the J-T theorem, if applied to 3d ions, in the orbital space only. A direct motivation for this paper is an erroneous claim of a recent Phys. Rev. Lett. **96** (2006) 027201 paper [1] that the high-spin (HS) state of the $3d^6$ configuration is not Jahn-Teller active. This erroneous conclusion was inferred by consideration of the high-spin HS state as ascribed by $t_{2g}^4 e_g^2$ ($S=2$) configuration with two e_g electrons. This situation was contrasting to the IS state, with one e_g electron following from a notation of the IS state as $t_{2g}^5 e_g^1$, as being J-T active, i.e. being a source of lattice distortions.

We look on the J-T effect as related to a tendency for the lowering energy of a system by the splitting and the lowering energy of the predominantly lowest ionic state. This splitting is an effect of lattice distortions or more generally of lower-symmetry charge distribution.

We argue that the J-T theorem has to be considered in the spin-orbital space. It is a direct consequence of the intra-atomic spin-orbit coupling which, though weak in the 3d ions, always exists. We are fully aware that we are not the first considering the spin-orbital space and

the spin-orbit coupling but the appearance of this paper in Phys. Rev. Lett. proves the need to remind this basic knowledge. Moreover, we would like to put here attention to a very large degeneracy of 3d states being as is known from the atomic physics as $\binom{10}{n}$. It is 10, 45, 120 and 210 for $n=1(9)$; $2(8)$, $3(7)$ and $4(6)$ d electrons, respectively. It is in a sharp contrast to commonly discussed 5 orbital states only. This large number of states in the free ion is grouped in electronic terms. The ground state is described by two Hund rules. The effect of the octahedral crystal field has been studied by Tanabe and Sugano already 50 years ago yielding well-known Tanabe-Sugano diagrams.

Figs 1c and 2c show the influence of the spin-orbit coupling on the localized states of the strongly-correlated $3d^n$ electron system produced by crystal-field interactions of the octahedral symmetry for the ground term described by two Hund's rules. It is worth to note that in a solid a different ground term can be realized. For instance, in LaCoO_3 the ground term is a many-electron subterm 1A_1 originating from the 1I term, which in the free Co^{3+} ion lies 4.45 eV above the ground term 5D [2]. The 13-fold degenerated 1I term is split by the octahedral crystal field and the subterm 1A_1 is strongly pushed down, by relatively strong crystal field, due to its very large orbital quantum number $L=6$, as occurs on the Tanabe-Sugano diagram for $Dq/B=2.025$. This atomic-scale singlet 1A_1 subterm with $L=6$ is a low-spin state $t_{2g}^6 e_g^0$ ($S=0$) which can be written also as $t_{2g\uparrow}^3 t_{2g\downarrow}^3$.

Inspecting Figs 1c and 2c one can conclude that practically all 3d ions are J-T ions, i.e. their electronic atomic-like structure in the octahedral surrounding is very sensitive to the detailed local symmetry. This prediction is in perfect agreement with experimental observations - everywhere where exact experimental studies are performed the octahedral surroundings is found to be distorted. Even NiO is distorted despite the NaCl structure and the orbital singlet ground state. An off-octahedral distortion and magnetic interactions remove fully atomic-

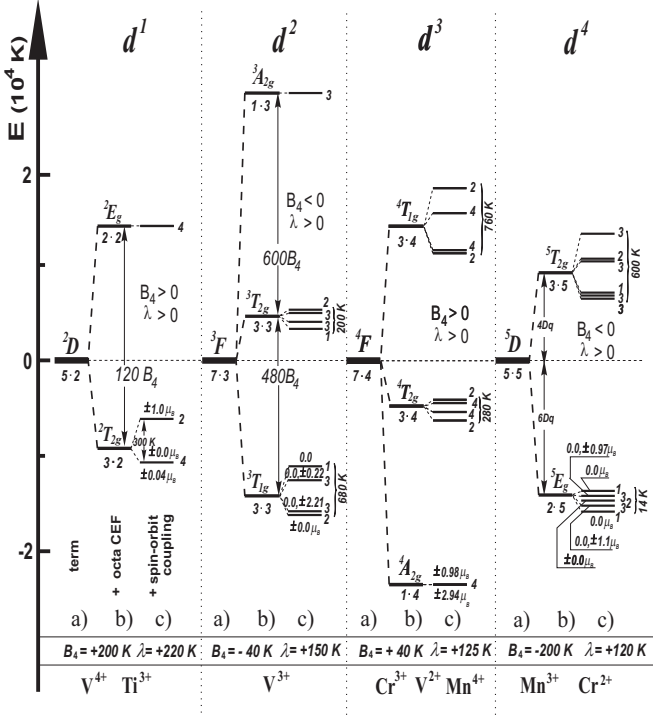


FIG. 1: The calculated electronic structure of the $3d^n$ configurations of the $3d$ ions, $1 \leq n \leq 4$, in the octahedral crystal field (b) and in the presence of the spin-orbit coupling (c). According to the Quantum Atomistic Solid-State theory the atomic-like electronic structures, shown in (c), are preserved also in a solid. (a) - shows the Hund's rule ground term. Levels in (c) are labeled with degeneracies in the spin-orbital space whereas in (b) the degeneracy is shown by the orbital-spin degeneracy multiplication. The spin-orbit splittings are drawn not in the energy scale which is relevant to CEF-only levels shown in figures b. On the lowest localized level the magnetic moment (in μ_B) is written. The shown states are many electron states of the whole d^n configuration. At zero temperature only the lowest state is occupied. The higher states become populated with the increasing temperature.

scale degeneracy [3]. The splitting of the 15-fold degenerated $^5T_{2g}$ subterm by trigonal distortion in the presence of the spin-orbit coupling has been presented in Ref. [4] for the Fe^{2+} ion in $FeBr_2$ together with the formation of the magnetic state below T_N of 14 K.

The demanded spin-orbital space for the consideration of the J-T theorem for $3d$ ions is consistent with the standard treatment of rare-earth-ion compounds.

In conclusion, we argue that the J-T theorem, if applied to $3d$ -ion compounds, has to be considered in the spin-orbital space.

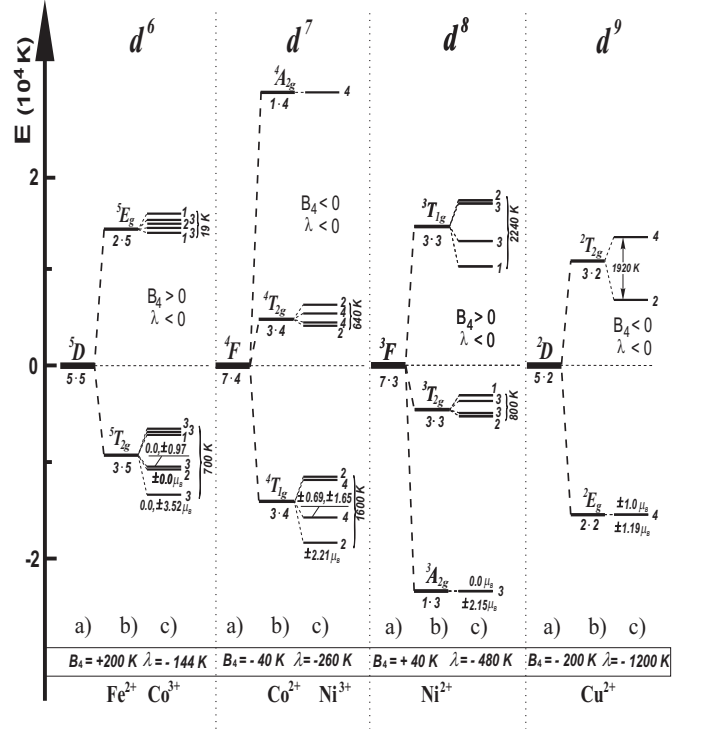


FIG. 2: The calculated electronic structure of the $3d^n$ configurations of the $3d$ ions, $6 \leq n \leq 9$, in the octahedral crystal field in the presence of the spin-orbit coupling. According to QUASST these atomic-like electronic structures are preserved also in a solid.

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